

Exercise walk-through

5.9

Pre-Equilibrium Approximation

AP Chemistry

You must be able to

- recognise when the slow step contains an **intermediate**
- substitute for the intermediate using the fast pre-equilibrium
- write a rate law with only reactants

1

The method

Method — The problem

If the **first** step is fast and reversible and the **second** (slow) step uses an **intermediate**, the raw rate law would contain that intermediate – which is not allowed.

Exercises 2.1·2.3

2.1 Why can't an intermediate stay in the final rate law? [1]

2.2 In a fast equilibrium, the forward rate equals the _____ rate. [1]

2.3 If $[\text{N}_2\text{O}_2] \propto [\text{NO}]^2$, and $\text{rate} = k[\text{N}_2\text{O}_2][\text{O}_2]$, write the rate in terms of reactants. [2]

Exercises 2.1-2.3

2.1 Why can't an intermediate stay in the final rate law? [1]

2.1

- It is not a measurable starting reactant; the rate law must be in terms of reactants
-

2.2 In a fast equilibrium, the forward rate equals the _____ rate. [1]

2.2

- reverse (backward)
-

2.3 If $[\text{N}_2\text{O}_2] \propto [\text{NO}]^2$, and $\text{rate} = k[\text{N}_2\text{O}_2][\text{O}_2]$, write the rate in terms of reactants. [2]

2.3

- $\text{rate} = k[\text{NO}]^2[\text{O}_2]$

Exercise 3.1

3.1 When the slow step contains an intermediate, you replace it using the [1]

☐

A overall equation

B fast pre-equilibrium step

C products

D activation energy

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A overall equation

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3.1 B

- the fast pre-equilibrium step

Exercise 3.2 (a)

3.2 Mechanism: Step 1 (fast) $A \rightleftharpoons B$ with $[B] \propto [A]$; Step 2 (slow) $B + C \rightarrow D$.

(a) Write the slow-step rate law.

[1]

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(a) Write the slow-step rate law.

[1]

(a)

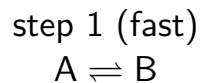
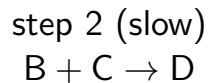
- $\text{rate} = k[B][C]$

Exercise 3.2 (b)

3.2 Mechanism: Step 1 (fast) $A \rightleftharpoons B$ with $[B] \propto [A]$; Step 2 (slow) $B + C \rightarrow D$.

(b) Substitute for the intermediate to give the overall rate law.

[2]

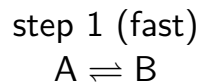
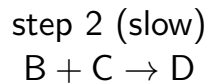


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[2]



(b)

- since $[B] \propto [A]$, rate = $k'[A][C]$

Exercise 3.3

3.3 Explain why a fast reversible first step is called a “pre-equilibrium”.

[2]

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3.3

- The fast reversible step reaches equilibrium **before** the slow step consumes its product, so an equilibrium is established ahead of the rate-determining step